Molecular-orbital Calculations for Clar's Hydrocarbon 1 : 13 : 12-6 : 16 : 7-*Dibenzonaphthacene* (*Zethrene*). *Part II*. The Diels–Alder Reaction.*

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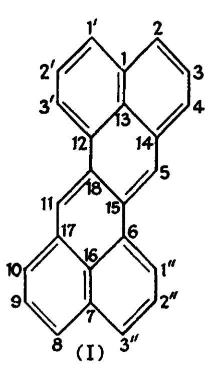
Molecular-orbital calculations for all the geometrically possible positions of attack in the Diels–Alder reaction of the polynuclear hydrocarbon 1 : 13 : 12-6 : 16 : 7-dibenzonaphthacene (Clar's zethrene) with maleic anhydride suggest that the reaction should proceed much more favourably for one pair of positions (1″ : 5 and 11 : 3′) than for any other position. This prediction, which has not yet been tested experimentally, correlates well with the free-valence data for this hydrocarbon.

We have recently discussed certain properties of the polynuclear hydrocarbon 1 : 13 : 12-6 : 16 : 7-dibenzonaphthacene (" zethrene "; I) using the simple molecular-orbital method (Coulson and Moser, *J.*, 1953, 1341). Now zethrene belongs to the class of condensed hydrocarbons which readily undergo Diels–Alder addition of maleic anhydride; it is known (see later) that this reaction does occur with zethrene, but the location of the points of attack are not known and it would be a problem of some considerable difficulty to characterise the positions in the molecule across which the addition takes place. This is a situation in which theoretical prediction may well prove exceedingly valuable; it is the object of this communication to report such predictions. For this purpose we use the theory originally proposed by R. D. Brown (*J.*, 1950, 691, 2730; 1951, 1612, 3129) to account for the Diels–Alder reaction between dienes and dienophiles. The formation of an adduct in this reaction, as, *e.g.*, between $C_{(2)}$ and $C_{(14)}$, or $C_{(5)}$ and $C_{(1'')}$, involves the removal from the resonating framework of the two centres at which addition occurs, and also the removal of two of the π-electrons. These are needed in the formation of the two new C–C bonds. It is convenient mathematically to regard this process as being achieved in two stages: (*a*) we localise two π-electrons on the appropriate atoms of the dienophile and thus remove these atoms from the conjugation path; (*b*) we subsequently use these two localised electrons to form the new bonds to the diene. The fundamental assumption of Brown's theory is that the relative ease of formation of the adduct at atoms m and n of the hydrocarbon, depends only on the energy required in stage (*a*), provided of course that m and n are of proper geometrical orientation for the reaction to take place. In the case of polynuclear hydrocarbons this condition is taken to imply that m and n are *para* to one another in the conjugated hydrocarbon. The para-localisation energy P which is thus involved, is defined by



(I)

$$P = E_r - E + 2\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where E is the π-electron energy of the original conjugated system, 2α is the energy of two isolated π-electrons (α is generally taken to be the arbitrary zero of the energy scale for each electron, in calculations of this kind), and E_r is the total π-electron energy of the " residual molecule." This " residual molecule " consists of the one or more separate conjugated systems left when the two carbon atoms m and n are isolated. Our object therefore is to calculate the localisation energy P. A comparison of P for different possible positions should show at once which is the most likely one for the reaction.

To calculate P we need E and E_r. In the simplest M.O. theory these are expressed in terms of the resonance integral β, where, in usual notation $\beta = \int\phi_i^* H\phi_j d\tau$, and all overlap integrals such as S ($\equiv\int\phi_i\phi_j d\tau$) are neglected. A better approximation includes S, and then computes E and E_r in terms of a new resonance integral γ, where $\gamma = \beta - S\alpha$. In the present work there is a particular reason for preferring the second approximation, for although the amount of quantitative experimental data reported in the literature for the

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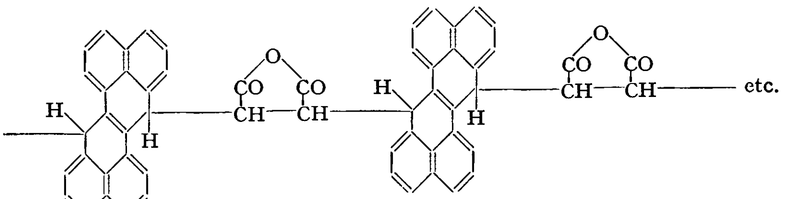
* The paper, *J.*, 1953, 1341, is considered as Part I.

Diels–Alder reaction is not extensive, the agreement between theory and experiment for certain derivatives of benzanthracene (Bachmann and Kloetzel, *J. Amer. Chem. Soc.*, 1938, **60**, 481) is almost quantitative when the energies are expressed in terms of γ, but only qualitative when in terms of β. In order to make these calculations at all simply, it was necessary to extend certain previous formulæ introduced by Coulson (*Proc. Camb. Phil. Soc.*, 1940, **36**, 201) and de Heer (*Phil. Mag.*, 1950, **41**, 370). In view of the wider application of these new formulæ, we have put them in the separate, following paper. We have taken S to be uniformly 0·25 for neighbouring atoms, and otherwise zero.

Clar and his collaborators have shown that the reaction takes place quite readily with zethrene; for the green colour of the solution of zethrene is rapidly discharged. But no information is available by this means about the structure of the adduct. There are in the main two possibilities, either that the adduct is a simple one-to-one complex as in other molecules so far studied, or, as was suggested to us by a referee, that it is a copolymer such as



We have only considered the first of these possibilities, despite the attractive nature of the second which allows zethrene to be attacked at its most reactive positions. This is because Dr. Clar, to whom we are much indebted for information about this reaction, tells us that he has so far found no evidence to suggest a polymer formation, and also the type of attack which we shall later be led to suggest is one already familiar in certain other reactions, in particular with perylene. We have therefore thought it worth while (*a*) to show by comparison of the localisation energy P for zethrene and other hydrocarbons that the reaction would be expected on theoretical grounds, and (*b*) to predict the structure of the adduct by a comparison of the P-values for all of the ten geometrically plausible positions. Our conclusion in both (*a*) and (*b*) is quite unambiguous.

The results of our calculations are shown in the Table. It is unnecessary to give many details of the technique used, since this is either quite standard, or else follows directly the procedure recommended in the paper which follows. A few comments, however, are reserved for the appendix. Columns 1 and 5 give the positions at which the addition is geometrically possible. These are arranged in such a manner that the sequence of P-values, shown in columns 2 and 6 in γ-units, is an increasing one. This means that the most likely positions are those at the top left, and the least likely are those at the bottom right. Columns 3 and 7 show P-values in β-units, and columns 4 and 8 give the sum of the corresponding free valences calculated from our previous molecular diagram for this molecule.

Diels–Alder reaction with zethrene.

Positions	$P(\gamma)$	$P(\beta)$	Sum of free valences	Positions	$P(\gamma)$	$P(\beta)$	Sum of free valences
1″ : 5	2·33	3·59	0·359	1″ : 7	3·48	4·56	0·251
3″ : 6	2·85	4·21	0·299	2″ : 16	3·58	4·61	0·231
8 : 17	3·00	4·29	0·278	9 : 16	3·68	4·64	0·230
7 : 10	3·43	4·53	0·270	16 : 18	4·10	5·01	0·305
6 : 11	3·47	4·40	0·349	15 : 17	4·29	5·36	0·258

An inspection of this Table shows that the position 1″ : 5 (or the equivalent 3′ : 11) is very considerably favoured. Since the difference in P-values appears as an exponent in the rate of reaction, this suggests very strongly that these are the positions of the adduct. Fortunately the same conclusion is reached even when P is expressed, by using the simpler theory, in terms of β instead of γ, and also when the sum of the appropriate free valences is used as criterion instead of localisation energies. Now there are reasons for believing that the free-valence values will control the early stage of such a reaction as this, and the localisation energy the later (*i.e.*, transition) stage. The complete agreement between the results of columns 2, 3, and 4 gives strong support to the correctness of the conclusion. (The sequence of P-values is almost unchanged in passing from the γ-scheme to the β-scheme, there being only one quite minor inversion. But the correlation with free valences, while still good, is nothing like so perfect.)

Quantitatively the value $2{\cdot}33\,\gamma$ (or $3{\cdot}59\,\beta$) does not indicate an exceedingly fast reaction. Brown has used the 9 : 10-positions of anthracene (the *meso*-positions), where $P = 3{\cdot}31\,\beta$, as a standard reaction rate, with respect to which other rates may be compared. On this basis the reaction would be expected to occur, but would only be about 10^{-6} as rapid as in anthracene. We are inclined to believe that this is not a very serious discrepancy: for in calculating E and E_r we have adopted the usual assumption of simple molecular-orbital theory, that all the β's and γ's are equal. Now our predictions of bond lengths (Table 2, Coulson and Moser, *loc. cit.*) indicate that the bonds $C_{(5)}$–$C_{(15)}$ and $C_{(6)}$–$C_{(1'')}$, both of primary importance for a reaction at the positions 5 : 1″, are probably somewhat shorter than most of the other bonds in the molecule. Also the bonds $C_{(1')}$–$C_{(2')}$ and $C_{(2'')}$–$C_{(3'')}$, which have to be converted into double bonds in the course of the localisation process, are already the most nearly double of all the bonds. This suggests that we could get improved quantitative results by proper modification of the various resonance integrals for these various bonds. Only a small change would be needed to cause considerable change in the predicted rate of reaction. We have not attempted to introduce such improvements because they would be most unlikely to alter calculated positions of attack, and better comparison with other values for different molecules reported in the literature is obtained if we keep to the standard resonance integrals. To make such changes is perfectly possible, but very laborious.

In all other polynuclear hydrocarbons so far investigated, Brown has found the reactive positions for Diels–Alder reaction to be the *meso*-positions of the anthracene-like part of the conjugated molecule. This is apparently not a general rule, for in zethrene the corresponding positions are 11 : 6 (or 5 : 12), and our calculations predict them to be fifth in order of decreasing probability. (But the free-valence criterion would make them second.)

NOTES ON THE NUMERICAL CALCULATIONS

In principle, the calculation of E_r presents no unusual difficulties, but in practice it is distinctly tedious to have to find all the roots of ten or more polynomials of the 22nd degree, with the aid of nothing more than a desk machine. Furthermore only the total energy, and not the individual energy values, was needed. For that reason we used formula (16) of the following paper. This expresses the energy E of any conjugated hydrocarbon in the form

$$E = \frac{2\sqrt{(Nn)}\gamma}{1 + Sx} + \frac{2\gamma}{\pi}\int_0^\infty \frac{1 - S^2t^2}{(1 + S^2t^2)^2} \ln \frac{\Delta(it)}{(t^2 + x^2)^n}\,dt,$$

where N = number of carbon-carbon bonds in the molecule, $2n$ = number of π-electrons in the system, $\Delta(\varepsilon)$ = secular determinant as a function of the energy ε, $x^2 = N/n$, $t = \varepsilon/\beta$, and $i^2 = -1$.

We first expanded the polynomials $\Delta(\varepsilon)$ for each of our ten residual molecules, and then evaluated them numerically from $k = 0$ to $k = 6$ at suitable intervals, using an I.B.M. punched-card machine model 602A. We used a floating-decimal scheme devised by one of us (M. P. B.). The remainder of the computation, which involved numerical integration from 0 to 6, a ten-strip formula from 9 to 2 and 2 to 6, and an asymptotic expression for the contribution to the integral from $t > 6$ being used, was carried through on a desk machine. We acknowledge the facilities for the earlier part of these calculations which were provided by the I.B.M. Company in London. We believe that our values for P in the Table are accurate to about 1 or 2 in the second decimal place.

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